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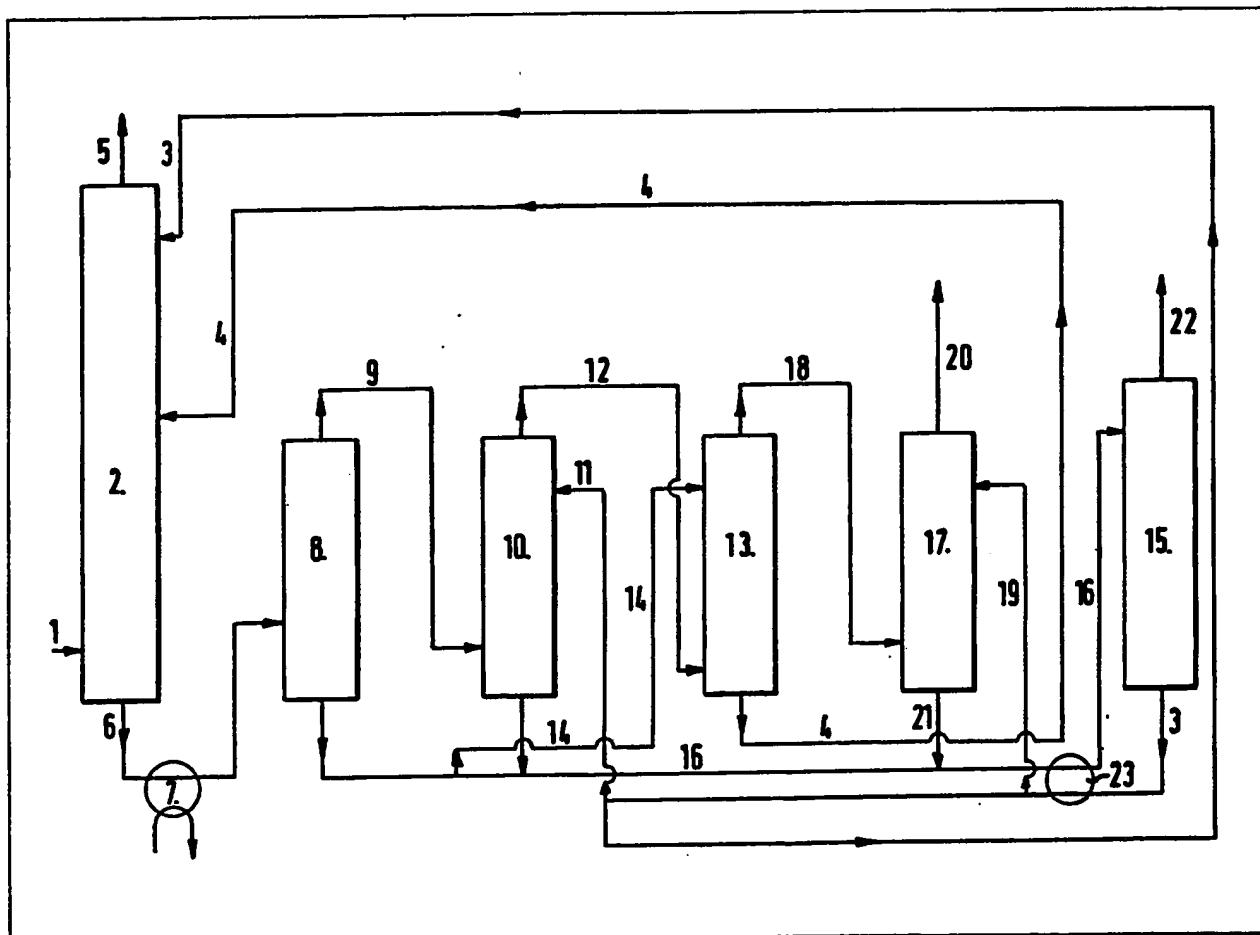
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(54) Process for the removal of H_2S and CO_2 from a gas mixture

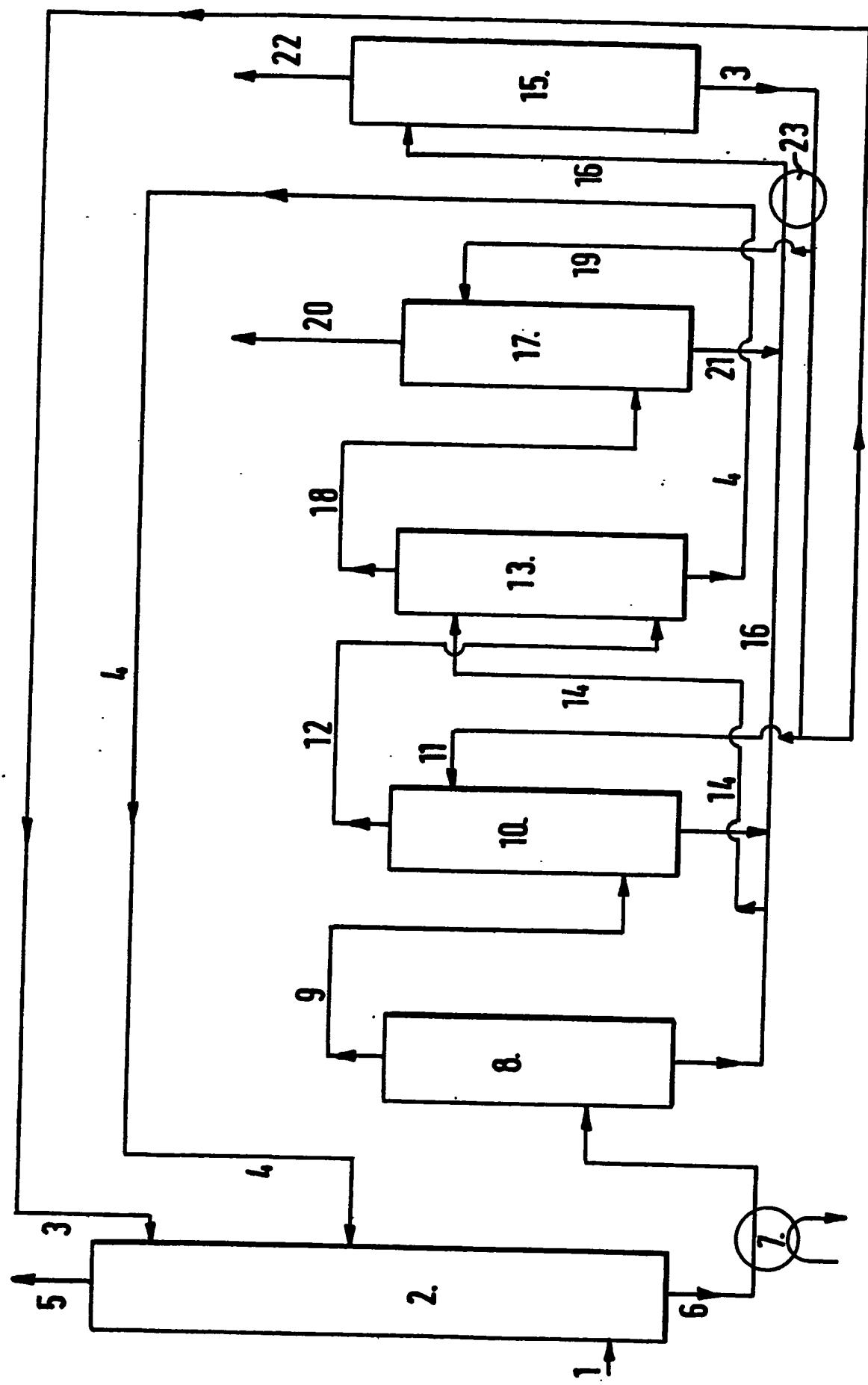
(57) A process for the removal of H_2S

and CO_2 from a gas mixture in which

- the gas mixture is contacted at elevated pressure countercurrently with lean solvent which comprises a tertiary amine and a physical absorbent;
- the loaded solvent obtained is flashed;
- the flash gas set free in step b) is contacted countercurrently with lean solvent under conditions which are selective for H_2S removal;
- part of the loaded solvent obtained after flashing is stripped with the gas obtained in step c);
- the stripped solvent obtained in step d) is introduced as semi-lean solvent in step a);
- the gas obtained in step d) is contacted countercurrently with lean solvent under conditions which are selective for H_2S removal, and
- loaded solvent obtained in steps c), b) and f) is regenerated to yield lean solvent and an H_2S -containing gas suitable for use in a Claus process.



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SPECIFICATION

Process for the removal of H₂S and CO₂ from a gas mixture

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The invention relates to a process for removal of H₂S and CO₂ from a gas mixture with simultaneous preparation of an H₂S-containing gas which is suitable for use in a Claus process.

10 In many cases it is necessary to remove H₂S and, if present, other sulphur-containing impurities such as COS from gas mixture, for example to render these gas mixtures suitable for catalytic conversions using sulphur-sensitive catalysts, or to reduce environmental pollution if the said gas mixtures or combustion gases obtained therefrom are discharged to the atmosphere.

15 Examples of gas mixtures from which H₂S and/or other sulphur-containing compounds generally have to be removed are gases obtained by partial combustion, or complete or partial gasification of oil and coal, refinery gases, town gas, natural gas, coke-oven gas, water gas, propane and propene.

20 In many cases the H₂S will be removed from the said gas mixtures using liquid solvents, which will often be basic. In a large number of cases the gas mixtures from which H₂S is to be removed will also contain CO₂, at least some of which will be absorbed in the liquid solvent together with H₂S. The H₂S and 25 CO₂ will be removed from the said gas mixtures at the pressure of the gas mixture concerned, i.e. in many cases at elevated pressure.

25 Although in most cases H₂S is to be removed nearly completely from the gas mixtures for the reasons given above, in many instances part or all of the CO₂ may remain in the gas mixtures after the removal of the H₂S therefrom, because CO₂ up till a certain extent does not hamper further use of the purified gas mixture. For that reason it would be 30 attractive to have a process in which the ratio of H₂S to CO₂ removed from the gas mixture can be controlled at will, or in other words, in which the selectivity of the removal of H₂S over CO₂ can be regulated at will.

35 In many H₂S removal processes known hitherto the removal of COS often gives rise to problems, because the COS is not absorbed to a great extent in the solvent; it would be attractive to have a method to overcome this problem.

40 The H₂S- and CO₂-containing gas obtained after regeneration of the solvent used for the removal of these so-called acid gases from the gas mixture cannot be discharged to the atmosphere before at least most of the H₂S has been removed therefrom.

45 The H₂S is very suitably removed from this gas by converting it to elemental sulphur, which is separated off. The conversion of H₂S into elemental sulphur is generally carried out in the art by means of a Claus process in which some of the H₂S is

50 oxidized to SO₂, and sulphur and water are formed by reaction of H₂S with SO₂, with or without the assistance of a suitable catalyst. In order to be able to carry out a Claus process, the molar percentage of

Claus process can be carried out by separating one-third part of the gas, combusting the H₂S therein to SO₂, and subsequently mixing the resultant SO₂-containing gas with the balance of the H₂S-

55 containing gas, after which the Claus reaction can be further carried out at elevated temperature and preferably in the presence of a catalyst. In case a Claus process is to be carried out with a gas which contains CO₂ and about 40% mol H₂S or more, the gas can be combusted with a quantity of air which is sufficient to convert one-third part of the H₂S into SO₂, and subsequent reaction of the H₂S and SO₂ to form sulphur and water.

60 Besides the suitability of a process for the removal of H₂S and CO₂ (and if desired COS) from gas mixtures, a feature of very much technical interest is the amount of energy needed for the process. The major amount of energy needed is used in the regeneration of the loaded solvent, which regeneration is in most cases carried out by stripping with steam. The steam requirement is greatly dependent on the amount of solvent circulating in the process, the lower the solvent circulation the lower the amount of steam needed for regeneration. The 65 extent of loading of the loaded solvent to be regenerated may also be of importance in this respect. A reduction in solvent circulation would also contribute to further capital savings in that smaller absorption and regeneration columns, smaller heat-exchange equipment and less solvent for filling the 70 columns suffice.

The invention provides a process in which H₂S and CO₂ are removed from a gas mixture with preparation of a gas suitable for use in a Claus process, in 75 which process the amount of CO₂ to be removed from the gas mixture can be regulated, COS can be removed from the gas mixture and the amount of solvent circulating in the process is limited.

Accordingly, the invention provides a process for 80 the removal of H₂S and CO₂ from a gas mixture with simultaneous preparation of an H₂S-containing gas which is suitable for use in a Claus process, which process is characterized in that

- a) the gas mixture is contacted at elevated 85 pressure countercurrently with a lean solvent which comprises a tertiary amine and a physical absorbent,
- b) the loaded solvent obtained is flashed by pressure release to a pressure which is below the sum of the partial pressures of CO₂ and H₂S in the 90 loaded solvent at the prevailing temperature,
- c) gas containing H₂S and CO₂ set free in step b) is contacted countercurrently with lean solvent under conditions which are selective for H₂S removal,
- d) the loaded solvent obtained in step c) is regenerated to yield lean solvent,
- e) part of the loaded solvent obtained after flashing in step b) is regenerated to yield lean solvent,
- f) part of the loaded solvent obtained after flashing in step b) is stripped with the gas obtained in step c),
- g) the stripped solvent obtained in step f) is

lean solvent,

h) the gas obtained in step f) is contacted countercurrently with lean solvent under conditions which are selective for H₂S removal,

5 5) j) the loaded solvent obtained in step h) is regenerated to yield lean solvent, the gas obtained at regenerations d), e) and j) yielding the H₂S-containing gas which is suitable for use in a Claus process.

10 A lean solvent in the context of this specification and claims is a solvent which is substantially free from H₂S and CO₂. A loaded solvent is a solvent which contains appreciable amounts of CO₂ and H₂S, and a semi-lean solvent is a solvent which 15 contains appreciable amounts of CO₂ but no or a limited amount of H₂S.

The solvent comprises a tertiary amine, a physical absorbent and preferably contains water.

H₂S and CO₂ are able to react with tertiary amines.

20 Very suitable tertiary amines are aliphatic, in particular those which contain at least one hydroxyalkyl group per molecule. Examples are triethanolamine, tripropanolamine, triisopropanolamine, ethyldiethanolamine, dimethylethanolamine, diethylethanolamine. Preference is given to methyldiethanolamine.

A physical absorbent is a compound in which H₂S and CO₂ are soluble, but without undergoing a reaction therewith. Very suitable physical absorbents are sulfolane and substituted sulfolanes, tetraethylene glycol dimethyl ether, alcohols with 1-5 carbon atoms per molecule (e.g. methanol), N-methylpyrrolidone, alkylated carboxylic acid amides (e.g. dimethylformamide). Preference is given to sulfolane. The word "sulfolane" denotes the compound "tetrahydrothiophene 1,1-dioxide".

The amounts of tertiary amine and physical absorbent (and if present water) in the solvent may vary between wide limits. Very suitably the solvent contains in the range of from 5 to 35% w of water, in 40 the range of from 15 to 55% w of physical absorbent, preferably sulfolane and in the range of from 10 to 60% w of tertiary amine, preferably methyldiethanolamine.

The contacting of the gas mixture with the solvent 45 in step a) is carried out at elevated pressure, which is considered to be a pressure of at least 5, in particular of at least 10 bar. Pressures in the range of from 20 to 100 bar are very suitable.

The contacting of the gas mixture with the solvent 50 in step a) is very suitably carried out in a zone which comprises in the range of from 15 to 80 contacting layers, such as valve trays, bubble cap trays, baffles and the like. It has surprisingly been found that by the process according to the invention, using a

55 solvent comprising a tertiary amine and a physical absorbent, the H₂S can substantially be removed from the gas mixture used as feed while regulating the amount of CO₂ which is left in the purified gas. This regulation can be achieved by regulating the 60 solvent circulation, i.e. the ratio of solvent fed to the extracting zone and the amount of gas mixture fed thereto.

The temperature and pressure during the contact-

of from 15 to 110°C are very suitable, temperatures in the range of from 20 to 80°C are preferred.

In step a) all or the greater part of COS present is removed from the gas mixture.

70 The loaded solvent obtained from step a) contains H₂S and CO₂ and may also contain appreciable amounts of dissolved non-acid components from the gas mixture to be purified, e.g. hydrocarbons, carbon monoxide and/or hydrogen. It may be of

75 advantage to remove these non-acid components at least partially from the loaded solvent by flashing to a pressure which is higher than the sum of the partial pressures belonging to the H₂S and CO₂ present in the loaded solvent. In this way only very small

80 amounts of H₂S and CO₂ are released from the solvent together with the non-acid components. If desired, the gas mixture obtained from this flashing may be recirculated to step a). In step b) the loaded solvent is flashed to a pressure which is below the

85 sum of the partial pressures of the CO₂ and H₂S present in the loaded solvent at the prevailing temperature, i.e. to a pressure in the range of from 5 to 1 bar. Flashing to about atmospheric pressure is preferred. In the gas set free during the flashing the

90 molar ratio of CO₂ to H₂S is higher than the molar ratio of the CO₂ and H₂S which remain present in the loaded solvent after the flashing. The flashing in step b) is very suitably carried out at a somewhat higher temperature than the contacting in step a), e.g. at a

95 temperature in the range of from 50 to 120°C, preferably at a temperature in the range of from 60 to 90°C. Heating of the loaded solvent before it is flashed is conveniently carried out with low-grade heat or by heat exchange with other process

100 streams, in particular with regenerated lean solvent.

The gas set free during the flashing substantially contains CO₂ and H₂S, and the H₂S is removed therefrom in step c) by contacting the said gas countercurrently with lean solvent. It is of advantage

105 to remove the H₂S selectively from this gas, and this very suitable achieved by contacting the said gas with lean solvent countercurrently in a tray column with at most 25 trays and at a gas velocity of at least 1/2 m/sec. The pressure applied in this step will in

110 general be that of the gas set free during the flashing. In order to achieve a good selective removal of H₂S the temperature of the lean solvent is very suitably in the range of from 15 to 50°C, although temperatures below or above this range are not

115 excluded. In order to reduce the amount of lean solvent required in step c) it is of advantage to lower the temperature of the gas set free during the flashing in step b), e.g. by cooling, before contacting it with lean solvent in step c).

120 The loaded solvent obtained in step c) is regenerated in step d) to yield lean solvent as will be discussed later.

The gas obtained in step c) is substantially free from H₂S and consists totally or for the greater part of CO₂.

125 The loaded solvent obtained after the flashing in step b) is split into two parts. The first part is regenerated in step e) to yield lean solvent as will be

after the flashing in step b) is stripped in step f) with the gas obtained in step c) which gas consists for the greater part, and in most cases totally, of CO_2 . In this way the loaded solvent obtained after the flashing is freed at least partly from H_2S but not from CO_2 , thus yielding semi-lean solvent.

This semi-lean solvent is in step g) introduced in step a) at a point nearer to the entrance of the gas mixture than the lean solvent. In doing so regeneration of this semi-lean solvent is avoided, thus leading to an appreciable energy saving, because no steam or other means are to be used for its regeneration. Moreover, the CO_2 present in this semi-lean solvent reduces the removal of CO_2 from the gas mixture, thus increasing the selectivity of the process for H_2S removal, which in many cases may be particularly attractive.

The gas obtained in the stripping in step f) contains H_2S and CO_2 . The former is to be removed therefrom before it can be vented to the atmosphere or combusted and the combustion gases vented to the atmosphere. In order to achieve H_2S removal the strip gas is contacted countercurrently with lean solvent in step h), preferably under conditions at which H_2S is selectively absorbed. These conditions are the same as discussed for step c). Here again it may be of advantage to cool the gas obtained in step f) before contacting it with lean solvent in step h).

The loaded solvent thus obtained is regenerated in step j) to yield lean solvent as will be discussed later. The gas emerging from step h) consists essentially of CO_2 and contains only very small amounts of H_2S . In most cases environmental regulations will allow it to be vented to the atmosphere; if desired, this gas

35 may be combusted and the combustion gases vented.

It is preferred that the loaded solvents to be regenerated in steps d), e), and j) are combined and regenerated together.

40 The regeneration is very suitably carried out by heating in a regeneration column (e.g. to a temperature in the range of from 80 to 160°C), which heating is preferably carried out with the aid of steam. The gas obtained during this regeneration has such an 45 H_2S content that it can suitably be used in a Claus process for the preparation of sulphur.

The lean solvent obtained after the regeneration will be introduced at the appropriate places in the system discussed above. It is very suitable to use the 50 regenerated solvent for heat exchange purposes before introducing it in steps a), c) and h); in particular the regenerated solvent is heat-exchanged with the loaded solvent obtained after the flashing step b) and/or with the loaded solvent emerging 55 from step a) before flashing.

The invention is further illustrated at the hand of the Figure which only shows one embodiment of the invention.

Gas mixture to be purified is fed via a line 1 to an 60 absorber 2, in which it is contacted with lean solvent introduced via a line 3 and semi-lean solvent introduced via a line 4. Purified gas is leaving the absorber 2 via a line 5. Loaded solvent is leaving the

to a pressure below the sum of the partial pressures of the CO_2 and H_2S present in the loaded solvent. The gases set free during the flashing are led via a line 9 to an absorber 10 and contacted with lean

70 solvent supplied via a line 11. The gas emerging from the absorber 10 is forwarded via a line 12 to a stripper 13 and used as strip gas for part of the loaded solvent obtained in the flash vessel 8, which part is introduced in the stripper 13 via a line 14. The 75 remainder of the loaded solvent obtained in the flash vessel 8 and the loaded solvent obtained in the absorber 10 are sent to a regenerator 15 via a line 16, in which line they are heat-exchanged with regenerated solvent from the regenerator 15. The semi-lean 80 solvent obtained in the stripper 13 is forwarded to the absorber 2 via the line 4.

The gas emerging from the stripper 13 is sent to an absorber 17 via a line 18 and contacted with lean solvent supplied via a line 19. The gas emerging 85 from the absorber 17 via a line 20 consists of CO_2 and no or a very small amount of H_2S . The loaded solvent emerging from the absorber 17 is forwarded via a line 21 to the line 16 and sent to the regenerator 15. Regeneration is carried out in the regenerator 15 90 by stripping with steam (not shown). The gas emerging from the regenerator 15 via a line 22 is rich in H_2S and is suitable for use in a Claus process. Regenerated solvent leaves the regenerator 15 via the line 3, is heat-exchanged in a heat exchanger 23 95 with loaded solvent in the line 16, and is fed to the absorbers 2, 10 and 17.

Example

The numbers refer to the Figure.

100 10,000 kmol/h of a gas mixture (which per 10,000 kmol contains 171 kmol H_2S , 4431 kmol CO_2 , 2775 kmol CO , 2578 kmol H_2 , 37 kmol N_2 and 8 kmol COS) are introduced at a temperature of 40°C and a pressure of 44 bar via line 1 into the bottom part of 105 absorber 2 (which contains 30 valve trays), and is countercurrently contacted with lean solvent consisting of methyldiethanolamine (50% w), sulfolane (25% w) and water (25% w), which solvent is introduced at a temperature of 40°C via line 3 (155 m³/h) at the top of the absorber, and with semi-lean 110 solvent (which contains 617 kmol/h CO_2 and 75 kmol/h H_2S) which is introduced at a temperature of 40°C and a pressure of 43.7 bar via line 4 (615 m³/h) on the third tray from above. Purified gas (8704.8 115 kmol/h composed of 3358 kmol CO_2 , 2753 kmol CO_2 , 2556 kmol H_2 , 37 kmol N_2 , 0.8 kmol COS and containing less than 200 ppm vol. H_2S) is leaving absorber 2 via line 5.

120 Loaded solvent is removed from absorber 2 via line 6 at a temperature of 68°C and at a pressure of 44 bar in an amount of 770 m³/h. This solvent contains 246 kmol/h H_2S and 1690 kmol/h CO_2 . It is heated in heater 7 with low pressure steam and flashed in flash vessel 8 to a pressure of 1.5 bar and a 125 temperature of 60°C. The gases set free are fed via line 9 to absorber 10 and contacted at 40°C and 1.4 bar with 200 m³/h lean solvent supplied via line 11. The gases emerging from absorber 10 are forwarded

vessel 8 (containing 140 kmol/h H₂S and 617 kmol/h CO₂) are introduced. The remaining loaded solvent from flash vessel 8 is heat exchanged in heat exchanger 23 with lean solvent and fed via line 16 to regenerator 15. The semi-lean solvent obtained from stripper 13 is introduced into absorber 2 via line 4 in the amount and at the temperature and pressure mentioned above. The gas emerging from stripper 13 is forwarded via line 18, and introduced into absorber 17, where it is contacted with 252 m³/h lean solvent, introduced via line 19 at a temperature of 30°C at 1.1 bar. Via line 20 770.5 kmol/h gas is emerging, from which gas 0.3 kmol consists of H₂S, 725.5 kmol of CO₂, 22 kmol of CO, 22 kmol of H₂ and 0.7 kmol of COS. The loaded solvent obtained from absorber 17 (252 m³/h containing 68.9 kmol/h H₂S and 120 kmol/h CO₂) is combined with the loaded solvents from flash vessel 8 and absorber 10 (together 607 m³/h) and forwarded via line 16 to regenerator 15, which is heated with steam. The gas which per hour emerges from regenerator 15 via line 22 (530.5 kmol) consists of 176.5 kmol H₂S, 353.3 kmol CO₂ and 0.7 kmol COS, the molar percentage of H₂S being 33%. Regenerated solvent (607 m³/h) is heat-exchanged in heat exchanger 23 with loaded solvent in line 16 and forwarded via line 3 to absorber 2 (155 m³/h), absorber 10 via line 11 (200 m³/h) and absorber 17 via line 19 (252 m³/h).

30 Comparative Experiment

10,000 kmol/h of the gas mixture used in the Example are introduced at a temperature of 40°C into the bottom part of an absorber, which contains 20 valve trays and is contacted countercurrently with a lean solvent consisting of diisopropanolamine (45% w), sulfolane (40% w) and water (15% w) (the use of which solvent is not according to the invention), introduced at a temperature of 40°C at the top of the absorber in an amount of 1675 m³/h, in order to yield purified gas containing less than 200 ppmv H₂S. Per hour this purified gas contains 1680 kmol CO₂. Loaded solvent is regenerated by stripping with steam, yielding a gas which consists of 2751 kmol/h CO₂ and 171 kmol/h H₂S, the molar percentage of H₂S being 5.9%.

The amount of loaded solvent to be regenerated (1675 m³/h) is much higher than that of the Example (607 m³/h), so that more steam is needed for its regeneration. Moreover the mixture of CO₂ and H₂S obtained at the regeneration of the loaded solvent is unsuitable for use in a Claus process, the H₂S content being too low. Further enrichment in H₂S by absorption/regeneration steps with a suitable solvent of this mixture is needed to produce a gas suitable for a Claus process.

CLAIMS

1. A process for removal of H₂S and CO₂ from a gas mixture with simultaneous preparation of an H₂S-containing gas which is suitable for use in a Claus process, characterized in that

a) the gas mixture is contacted at elevated

- b) the loaded solvent obtained is flashed by pressure release to a pressure which is below the sum of the partial pressures of CO₂ and H₂S in the loaded solvent at the prevailing temperature,
- 70 c) gas containing H₂S and CO₂ set free in step b) is contacted countercurrently with lean solvent under conditions which are selective for H₂S removal,
- d) the loaded solvent obtained in step c) is regenerated to yield lean solvent,
- 75 e) part of the loaded solvent obtained after flashing in step b) is regenerated to yield lean solvent,
- f) part of the loaded solvent obtained after 80 flashing in step b) is stripped with the gas obtained in step c),
- g) the stripped solvent obtained in step f) is introduced as semi-lean solvent in step a) at a point nearer to the entrance of the gas mixture than the 85 lean solvent,
- h) the gas obtained in step f) is contacted countercurrently with lean solvent under conditions which are selective for H₂S removal,
- j) the loaded solvent obtained in step h) is 90 regenerated to yield lean solvent,
- the gas obtained at regenerations d), e) and j) yielding the H₂S-containing gas which is suitable for use in a Claus process.

2. A process according to claim 1, characterized in that the solvent contains water.

3. A process according to claim 1 or 2, characterized in that the tertiary amine is aliphatic and contains at least one hydroxyalkyl group per molecule.

100 4. A process according to claim 3, characterized in that the tertiary amine is methyldiethanolamine.

5. A process according to any one of the preceding claims, characterized in that the physical absorbent is tetrahydrothiophene 1,1-dioxide.

105 6. A process according to any one of the preceding claims, characterized in that the solvent contains methyldiethanolamine, tetrahydrothiophene 1,1-dioxide and water.

7. A process according to claim 6, characterized in that the solvent contains in the range of from 10 to 60% w of methyldiethanolamine, in the range of from 15 to 55% w of tetrahydrothiophene 1,1-dioxide and in the range of from 5 to 35% w of water.

8. A process according to any one of the preceding claims, characterized in that in step a) the gas mixture is contacted with lean solvent in a contacting zone which comprises in the range of from 15 to 80 contacting layers.

9. A process according to any one of the preceding claims, characterized in that step a) is carried out at a contacting temperature in the range of from 20 to 80°C.

10. A process according to any one of the preceding claims, characterized in that step a) is carried out at a pressure in the range of from 20 to 100 bar.

11. A process according to any one of the preceding claims, characterized in that in step b) the

preceding claims, characterized in that the flashing in step b) is carried out at a temperature in the range of from 60 to 90°C.

13. A process according to any one of the 5 preceding claims, characterized in that as well in step c) the gas set free in step b), as in step h) the gas obtained in step f) is contacted with lean solvent countercurrently in a tray column with at most 25 trays at a gas velocity of at least $1/2$ m/sec.

10 14. A process according to any one of the preceding claims, characterized in that steps c) and h) are carried out at a contacting temperature in the range of from 15 to 50°C.

15 15. A process according to any one of the preceding claims, characterized in that the loaded solvents of steps d), e) and j) are combined and regenerated together.

16. A process according to any one of the preceding claims, characterized in that the regeneration is carried out by heating the loaded solvent in a regeneration column with steam to a temperature in the range of from 80 to 160°C.

20 17. A process according to any one of the preceding claims, characterized in that the regenerated solvent is heat-exchanged with loaded solvent emerging from step b) and/or step a) before being introduced in steps a), c) and h).

25 18. A process as claimed in claim 1, substantially as hereinbefore described, with reference to the 30 Example.

19. Gas mixtures from which H_2S and CO_2 have been removed by means of a process as claimed in any one of the preceding claims.

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